



Heterogeneous titanium catalysts for oxidation of dibenzothiophene in hydrocarbon solutions with hydrogen peroxide: On the road to oxidative desulfurization



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ABSTRACT

Titanium centers grafted on hydrophobic silica bearing long chain silanes (octadecyl or octyl) are able to oxidize dibenzothiophene (DBT), as well as simpler sulfides and 2,6-dimethyldibenzothiophene, to the corresponding sulfone in hydrocarbon solution with aqueous hydrogen peroxide in only a slight excess over the stoichiometric amount, without using any surfactant or cosolvent. The productivity per gram of catalyst or per Ti site can be optimized by tuning the silanization of the silica (or using a commercially available silanized silica) and the Ti loading of the catalyst. The catalyst preparation and the oxidation reaction are compatible with the use of an industrial grade aromatic solvent.

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1. Introduction

Environmental concerns make restrictions to the sulfur content of fuels more and more exigent [1]. The most important method for removing sulfur compounds from fuel is hydrothermal desulfuration (HDS) but a part of organic sulfur compounds is not easily removed and very high temperature and pressure conditions should be used to remove these recalcitrant sulfur compounds [2] making the HDS process very expensive. Alternative desulfuration strategies are currently envisaged and oxidative desulfuration (ODS) is one of the most interesting [3–6]. In the ODS process, the organic sulfides are oxidized to the corresponding sulfoxides and sulfones, that are in turn removed by extraction, adsorption, distillation or decomposition [6]. Although several oxidants, such as ozone or nitrogen oxides, have been tested [5], alkyl hydroperoxides, molecular oxygen, and hydrogen peroxide are undoubtedly the most interesting ones from environmental and economic points of view. The ideal system should use heterogeneous catalysts and

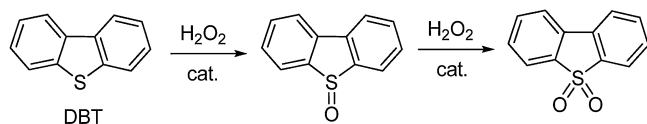
many efforts have been devoted to the development of processes using robust and recyclable catalysts.

Oxidations with molecular oxygen have been described with Mn–Co [7], Fe [8], or Pd [9], and very recently with V [10] catalysts. The reactions must be carried out either with pure oxygen and/or at high temperature, and in some cases the oxidation of aromatic hydrocarbons was detected [9]. Very recently a two-step oxidation has been described, by firstly generating benzylic hydroperoxides in the diesel with air on Cu catalysts and subsequent use of them as secondary oxidants in the oxidation of sulfur compounds with Mo catalysts [11]. Also very recently a metal-free method, with *N*-hydroxyphthalimide as catalyst in ionic liquid solution, has been described [12]. Alkyl hydroperoxides have been used in the continuous flow oxidation of sulfur compounds in fuels combined with Mo [13,14], Ti [15] and W [16] heterogeneous catalysts at 80–100 °C.

Hydrogen peroxide is one the most interesting oxidants, as it only generates water as concomitant product. One of the main problems related to the use of hydrogen peroxide in ODS is related to the presence of two reaction phases: an oily phase containing the sulfur compounds and an aqueous phase containing the oxidant. Hydrogen peroxide has been used for in-situ generation of peracids in combination with simple carboxylic acids, such as formic [17]

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Scheme 1. Oxidation of dibenzothiophene (DBT) with hydrogen peroxide.

or acetic [18], or more recently with functionalized ionic liquids acting also as extracting medium [19]. Different solid catalysts, based on V [20], Mo [21] or Re [22], have been tested, as well as Fe salts in combination with ionic liquids in a biphasic liquid system [23]. However, tungstates and tungsten based polyoxometallates are probably the most commonly used catalysts for oxidation with hydrogen peroxide. When the catalyst is in solution, it requires the use of a co-solvent, acetonitrile in most cases [24] to extract the sulfur compound allowing the reaction to proceed in the polar phase, or more commonly the use of a surfactant, either added [25–29], in the form of counter-ion of the polyoxometallate [30–32] or as ionic liquid phase [33,34]. The use of a co-solvent is also described in the cases of heterogeneous W catalysts [35–37].

Given the efficiency of Ti catalysts in oxidation reactions, several authors have described their application to ODS processes, for example TS-1 zeolite [38–40], Ti–HMS silica [38,41,42], a Ti–HMS/TS-1 composite [43], Ti–MCM48 [44], and TiO₂ nanotubes [45]. In all cases a co-solvent was also used, either methanol or acetonitrile, and the comparison between the efficiency of the catalysts in a monophasic or biphasic liquid medium have shown the problems associated to the presence of two immiscible liquid phases [45]. Some years ago, we developed a family of easily-prepared Ti-catalysts supported on amorphous silica, able to oxidize organic sulfides with both TBHP and hydrogen peroxide [46]. These catalysts have been further improved to allow an efficient epoxidation of alkenes with diluted hydrogen peroxide [47–49] showing that the hydrophobic character in the near environmental of the Ti–Lewis acid site is crucial to improve the results [48].

Therefore we considered it interesting testing our Ti-catalysts, designed to improve the epoxidation of bulky hydrophobic organic compounds with aqueous hydrogen peroxide, in the ODS of fuels with this oxidant. In this paper we report our preliminary results in the oxidation of a model compound, dibenzothiophene (DBT, Scheme 1), with aqueous H₂O₂ under conditions close to those that will be found in ODS process of real samples.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Preparation of the hydrophobic support

Merck 60 silica (10 g) was dried under vacuum at 140 °C overnight. To a suspension of this support in anhydrous toluene (50 mL) was added dimethyloctadecylsilyl chloride (10.4 g, 30 mmol) and the mixture was heated under reflux for 12 h under inert atmosphere. The resulting solid was filtered, washed with toluene (2 × 25 mL), ethanol (2 × 50 mL), water (until neutral pH), ethanol (2 × 50 mL), and ether (1 × 50 mL) and dried under vacuum at 140 °C overnight.

2.1.2. Grafting of the titanium precursor

To a suspension of the pre-treated support in anhydrous toluene (7 mL/g of solid), Ti(OⁱPr)₄ (1 mmol/g of solid) was added and the mixture was heated under reflux for 24 h under inert atmosphere. After cooling at room temperature, the solid was decanted and the supernatant was eliminated via syringe. The same volume of anhydrous toluene was added, the mixture was stirred for 10 min, the

solid was decanted and the supernatant was eliminated via syringe. The process was repeated 3 times. The solid was finally filtered, washed with dichloromethane and dried under vacuum.

A hydrophilic catalyst was prepared by treatment of Merck 60 silica, dried under vacuum at 140 °C overnight, with Ti(OⁱPr)₄ under the same conditions described above.

2.1.3. Variations in the catalyst preparation

Different solids were prepared by changing the nature of silane (dimethyloctylsilyl chloride), the amount of silane, the use of a reversed-phase silica (Polygoprep 60-130C₁₈ from Macherey–Nagel), the solvent (ShellSol A150, a mixture of C₉–C₁₀ alkyl aromatic hydrocarbons), and the amount of titanium precursor, as detailed in Table 2.

2.2. Characterization

Carbon analyses were carried out using a PerkinElmer 2400 elemental analyzer. Titanium analyses were carried out by plasma emission spectroscopy on a PerkinElmer Plasma 40 emission spectrometer. N₂ adsorption–desorption isotherms were determined on a Micromeritics ASAP 2000 apparatus. Surface area was determined by the BET method at low relative pressure (0.05 < P/P₀ < 0.20). Single point total pore volume was determined at P/P₀ = 0.99. Pore size distribution was calculated with the desorption branch of the isotherm by the BJH method. DR-UV spectra (200–700 nm) were recorded on a Unicam UV-4 spectrometer equipped with a Spectralon™ RSA-UC-40 Labsphere integrating sphere. For the polarity determination a green solution of Reichardt's dye (10^{−4} M) in anhydrous dichloromethane was added drop wise on the pre-dried (140 °C under vacuum) solid until the solid showed a color different from that of the solution. The solvent was evaporated under reduced pressure and the DR-UV spectrum (200–700 nm) was recorded immediately. Deconvolutions were carried out with Peakfit 4.0 program.

2.3. Oxidation procedures

2.3.1. Preliminary tests

To a solution of dibenzothiophene (DBT, 147.2 mg, 0.8 mmol) in isooctane (18 mL) was added the catalyst (see amount in Table 1) and the mixture was heated in a silicone bath at 60 °C. H₂O₂ (see concentration and amount in Table 1) was added dropwise (around 5 min) in one or several portions (see Table 1). The DBT conversion was monitored by GC, as most of the sulfone precipitated at room temperature. After 8 h, the reaction was stopped, the mixture of catalyst and dibenzothiophene sulfone was filtered off and washed with dichloromethane to dissolve the sulfone. The combined filtrates were analyzed by GC and ¹H NMR. In some cases the dichloromethane solution was evaporated separately to determine the isolated sulfone yield. The isooctane filtrate was washed with water (18 mL) and each phase was evaporated and analyzed by ¹H NMR separately.

2.3.2. Optimization of the catalyst

The reactions were carried out with 10 mg catalyst following the same method described above, but ShellSol A150 was used as a solvent, instead of isooctane. 60% H₂O₂ (1.6 mmol) was added dropwise (5 min) and reaction was monitored by GC. After 24 h, the same amount of oxidant was added and the reaction was left to proceed until a total reaction time of 72 h.

Table 1Reaction conditions and results in the oxidation of DBT with aqueous H₂O₂ catalyzed by hydrophobic Ti–silica (T-18H-1).^a

Entry	Mass of catalyst ^b	Total eq. H ₂ O ₂	Concentration of H ₂ O ₂	Additions of H ₂ O ₂ ^c	Sulfone yield (%) ^d
1	200 (9%)	2	10%	1	87 (4)
2	100 (4.5%)	2	10%	1	89 (1)
3	50 (2.2%)	2	10%	1	81 (1)
4	10 (0.45%)	2	10%	1	69
5	50 (2.2%)	5	10%	1	>99
6	10 (0.45%)	4	10%	1	68 (2)
7	10 (0.45%)	5	10%	5 (1 eq.)	79
8	10 (0.45%)	5	5%	5 (1 eq.)	32
9	10 (0.45%)	5	10% + 60% ^e	3 (1 + 2 + 2 eq)	>99
10	10 (0.45%)	5	10% + 70% ^e	3 (1 + 2 + 2 eq)	>99
11	10 (0.45%)	4	60%	2 (2 eq.)	>99
12	10 (0.45%)	2.5	60%	1	>99
13	–	2.5	60%	1	0

^a Reaction conditions: 0.8 mmol DBT, 18 mL isooctane, 60 °C, 8 h. For properties of catalyst, see Table 2.^b In parenthesis, the mol% of Ti used in the reaction.^c Number of dropwise (5 min) additions and equivalents added in each one.^d Determined by NMR in the crude. In parenthesis, the sulfoxide yield when detected.^e Concentration of H₂O₂ in the first addition and in the successive ones.**Table 2**Parameters of the synthesis of different Ti–silica catalysts and results of the analysis of the solids.^a

Catalyst	Preparation conditions		Amount (mmol/g)			
			Analysis (mmol/g)			
	Solvent	Silane	Silane	Ti(O ⁱ Pr) ₄	Silane ^b	Ti
T-18H-1	Toluene	C ₁₈ -SiMe ₂ -	3	1	0.504	0.365
T-18L-1	Toluene	C ₁₈ -SiMe ₂ -	0.6	1	0.237	0.835
S-18H-1	ShellSol	C ₁₈ -SiMe ₂ -	3	1	0.524	0.394
S-18M-1	ShellSol	C ₁₈ -SiMe ₂ -	1.5	1	0.573	0.329
S-18L-1	ShellSol	C ₁₈ -SiMe ₂ -	0.6	1	0.399	0.497
T-8H-1	Toluene	C ₈ -SiMe ₂ -	3	1	0.738	0.362
T-18H-0.2	Toluene	C ₁₈ -SiMe ₂ -	3	0.2	0.598	0.218
T-18L-0.2	Toluene	C ₁₈ -SiMe ₂ -	0.6	0.2	0.237	0.199
T-C18-1	Toluene	C ₁₈ HPLC ^c	-	1	0.388	0.648
T-C18-0.6	Toluene	C ₁₈ HPLC ^c	-	0.67	0.392	0.537
S-C18-0.6	ShellSol	C ₁₈ HPLC ^c	-	0.67	0.395	0.437

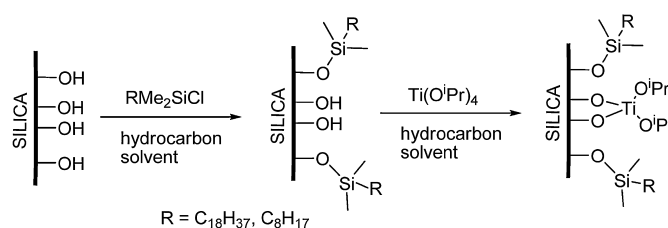
^a Solvent: used both in silanization and Ti grafting. Amount: mmol of reagent per gram of initial silica.^b Estimated from the carbon analysis of the solid, considering an average of 2 isopropoxy groups per Ti center.^c Catalyst prepared with Polygoprep 60-130C₁₈ from Macherey–Nagel.

3. Results and discussion

3.1. Preliminary tests

As general requirements for the catalyst, it should be solid to be easily separated, able to activate aqueous hydrogen peroxide in a hydrophobic environment (a complex mixture of hydrocarbons), that means in a biphasic liquid converted into a triphasic (solid–liquid–liquid) system once the catalyst is added, and finally it should be easy to prepare and not expensive.

Dibenzothiophene (DBT) was selected as probe molecule, as it is the simplest member of the family of compounds responsible for the difficulties in reaching the ultra-deep desulfurization. The hydrocarbon solvent chosen in a first set of experiments was isooctane, due to simplicity, boiling point and availability. From the experience of our group we knew that catalysts of titanium on silica were effective in hydrogen peroxide activation for oxidation reactions, such as epoxidation [47–49] and also sulfide oxidation under monophasic conditions, using methanol as the solvent for sulfides [46]. However, the same Ti–silica able to oxidize dibenzothiophene in methanol at 60 °C with the stoichiometric amount of H₂O₂ (2 eq) was not active under biphasic liquid conditions. The hydrophilic nature of the silica surface was considered as detrimental for such reaction, and then the support was made hydrophobic by functionalization with dimethyloctadecylsilane before titanium grafting (Scheme 2). The carbon analysis of this support shows a

**Scheme 2.** Preparation of hydrophobic titanium on silica catalysts.

functionalization of 0.53 mmol of silane per gram, and the textural properties of Merck 60 silica (surface area 512 m²/g, pore volume 0.816 cm³/g, mean pore diameter 62.8 Å) are modified up to values of 315 m²/g, 0.499 cm³/g, and 55.1 Å, in agreement with an important coverage of the surface with the hydrophobic silane [48]. The hydrophilic/hydrophobic character can be estimated by the DRUV spectrum of adsorbed Reichardt's dye [50], whose λ_{max} is shifted by the hydrogen-bond donating ability of the surface [51,52]. The value of λ_{max} at 515 nm in the starting silica suffers a bathochromic shift to 610 nm after silanization. The E_T^N polarity parameter calculated from those λ_{max} are 0.765 and 0.500 for silica and silanized silica respectively, similar to that of methanol and a longer chain alcohol such as 1-decanol, demonstrating the more hydrophobic character of the new support. In this way the concentration of

hydrocarbon solution around the catalyst should be high, while keeping the high local hydrophilic character of the titanium centers.

After Ti grafting, the hydrophobic catalyst (labelled T-18H-1, see below) had a Ti loading of 0.36 mmol/g. As a first result, it led to a 75% of productive use of H_2O_2 , with 70% yield of sulfone and 10% yield of sulfoxide. As a next step, the reaction conditions were optimized, namely the amount of catalyst and different parameters related to the oxidant, such as concentration in water, oxidant/substrate molar ratio, and addition method. The reaction temperature (60 °C) and the DBT concentration in isooctane (0.8 mmol in 18 mL, around 1400 ppm of S) were kept constant. The summary of the reaction conditions and the results is collected in Table 1.

As can be seen, high sulfone yields can be obtained with the stoichiometric amount of diluted (10%) H_2O_2 when the catalyst is used in high amount (entries 1 and 2), accounting for a 90% of productive use of the oxidant. As a practical remark, the reaction mixture can be easily fractioned. After filtration, the solid contains the catalyst and precipitated sulfone, which can be dissolved in dichloromethane, obtaining in this way 80% of isolated yield. The biphasic filtrate can be separated by decantation and the organic phase is washed with the same volume of water. In the organic phase 6% of unreacted DBT is recovered, together with 2% of sulfone. In the aqueous phase 4% of sulfone with 1% of sulfoxide are obtained. In that way the overall mass balance is more than 90%.

Lower amounts of catalyst require over stoichiometric diluted H_2O_2 to reach high sulfone yields (entries 3 and 5). However, when very tiny amount of catalyst is used (0.45 mol%), the increase in the amount of oxidant has not a significant impact on sulfone yield (entries 4 and 6). A possible kinetic competition of the unproductive decomposition of H_2O_2 may be the reason for this, and hence the system of oxidant addition was also explored, as this point had been crucial in the case of alkene epoxidation [47]. However, the addition of the 5 equivalents of H_2O_2 in five portions (entry 7) had not the expected influence, and only a minor improvement in sulfone yield was observed. On the contrary the dilution of the oxidant showed to have a very negative effect (entry 8). Hence, more concentrated H_2O_2 was used in the successive additions (entries 9 and 10), allowing in this way the total conversion to sulfone. In fact, the use of 60% H_2O_2 seemed to be optimal, leading to total conversion to sulfone in a single addition with only 2.5 equivalents of oxidant (entry 12).

Additionally the same system gave also total conversion with two simple sulfides, diphenylsulfide and methyl phenyl sulfide, and 75% conversion of 2,6-dimethyldibenzothiophene to sulfone. The sterically hindered sulfide group accounts for this lower conversion.

It should be noted that these results are obtained with only a 0.45 mol% of active metal, in contrast with the much higher amount used in other cases, up to more than 50 mol% Ti [43] or 75 mol% V [10].

3.2. Modifications of the catalyst

Several parameters in the preparation of the catalyst were modified in order to optimize its preparation, both from the point of view of the catalytic activity and the economy of the process. First of all, as a surface with hydrophobic character is needed, the covering degree of the surface was considered, as well as the minimum amount required of silyl chloride to reach that degree, as well as the chain length of the silane ($R = \text{C}_{18}\text{H}_{37}$ or C_8H_{17} , Scheme 2). Additionally, as reversed-phase HPLC silicas are functionalized with the same type of silanes, Polygoprep 60-130C₁₈, a support with similar textural properties (surface area, pore volume, pore size and particle size) as Merck 60 silica, was used for the sake of comparison. A second important parameter is the titanium loading, as it

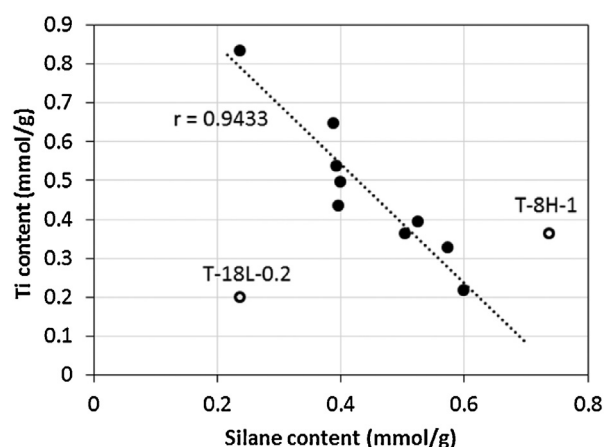


Fig. 1. Correlation between the Ti content and the silanization degree of the silica support.

is known that well-dispersed sites are more efficient in oxidation reactions [53] but a higher loading is more interesting from a practical point of view. The minimum amount of titanium precursor required for the optimal functionalization is also a crucial economical point. Finally, the catalysts are in general prepared in toluene suspensions, using a high purity solvent. The possibility of using an industrial degree solvent was also explored. The solids have been represented with a code X-YY-Z that includes the information about all those parameters:

- X = solvent in both preparation steps (T for toluene, S for ShellSol A150).
- YY = silane and amount (18 for octadecyl, 8 for octyl, H for high amount (3 mmol/g), M for medium amount (1.5 mmol/g), L for low amount (0.6 mmol/g), C18 for commercial HPLC silica).
- Z = amount of Ti (mmol Ti/g).

These points are summarized in Table 2, together with the analysis of the final solids. The amount of silane was estimated from the carbon analysis, considering an averaged titanium species containing two isopropoxy groups.

As can be seen in Table 2, the silanization with C18 reaches at maximum values of 0.5–0.6 mmol/g using the highest amount of silane, whereas the lowest (5 times less) is able to reach around 0.4 mmol/g, indicating that the cost of silane can be clearly optimized. The variations observed in the silane content might be due to different degrees of moisture on silica or in the solvent (toluene or Shellsol). In the case of C8, the maximum amount is significantly higher, around 0.7 mmol/g, probably due to the lower steric hindrance around the silane. The silanization degree controls the maximum titanium content, when an excess of Ti precursor is used in the preparation of the catalyst. As can be seen in Fig. 1, a good correlation is obtained between the Ti and silane contents, and the total silane + Ti loading is always around 0.9–1.1 mmol/g, which seems to be the result of a total covering of silica surface. The only two exceptions are obtained when low amounts of both silane and Ti precursor are used (T-18L-0.2), and hence the surface silica is not fully covered, and in the case of using the octylsilane (T-8H-1), because total covering is higher than expected, probably because of a more efficient packing of the smaller silane molecules, due to lower steric hindrance.

3.3. Catalytic results

In the preliminary part of this work, isooctane was used as surrogate of the diesel mixture of alkanes and cycloalkanes. How-

Table 3Results in the oxidation of DBT with H₂O₂ (60%) catalyzed by hydrophobic Ti–silica catalysts.^a

Catalyst	Productivity (mmol/g) ^b			TON ^c		
	3 h	24 h	72 h ^d	3 h	24 h	72 h ^d
T-18H-1	23.4	40.1	59.0	64.2	109.7	161.6
T-18L-1	36.0	44.7	56.8	43.2	53.5	68.0
S-18H-1	17.5	35.1	63.6	44.5	89.1	138.9
S-18M-1	21.0	38.2	54.7	63.7	116.1	193.3
S-18L-1	16.5	21.5	28.7	33.2	43.2	57.8
T-8H-1	25.5	46.9	62.1	70.6	129.7	171.6
T-18H-0.2	24.8	47.2	62.5	113.6	216.8	286.8
T-18L-0.2	25.0	41.6	54.7	124.7	207.7	272.9
T-C18-1	42.6	57.9	77.8	65.6	89.3	120.0
T-C18-0.6	31.2	49.7	77.2	58.1	92.6	143.7
S-C18-0.6	32.4	47.2	79.2	74.1	107.9	181.1

^a Reaction conditions: 0.8 mmol DBT, 18 mL ShellSol A150, 10 mg catalyst, 60 °C; dropwise addition (5 min) of 1.6 mmol H₂O₂ (60%). The same amount was added after 24 h.

^b mmol of DBT converted per gram of catalyst.

^c Mol of DBT converted per mol of Ti.

^d Final results with 4 eq. H₂O₂.

ever, diesel also contains a large fraction of aromatic hydrocarbons (30–35%), and most of them are alkyl substituted benzenes [54]. In order to check if this type of compounds would be detrimental for the oxidation method, ShellSol A150 was used as reaction solvent in this part of the work. ShellSol A150 is composed by a mixture of alkylated benzenes (C₉–C₁₆) obtained from petroleum distillates, very similar to the aromatic content of diesel and hence closer to the real samples for ODS. It is noteworthy that no changes in the composition of ShellSol A150 were observed in any of the oxidation reactions. All the rest of reaction conditions were kept as shown in the optimization, 0.8 mmol of DBT in 18 mL of solvent, 10 mg of catalyst at 60 °C, with two additions of H₂O₂ (60%, 2 eq. each). Unfortunately, it was not possible to monitor all the results of the reaction, as the sulfoxide and mainly the sulfone are not fully soluble in the reaction medium, which produces inaccuracies in the sampling. Thus, only the DBT conversion was monitored and two results were taken into account, firstly the productivity of the catalyst, considered as mol of DBT converted per gram of solid, and secondly, given that the substrate/Ti molar ratio varies due to the different Ti content of the catalysts (Table 2), the TON calculated as mol of DBT converted per mol of Ti site. The results at three different reaction times are collected in Table 3, one at short reaction time as representative of the catalytic activity, another one after 24 h, as representative of the efficiency in productive H₂O₂ use (both results also represented in Fig. 2), and finally after 72 h and the addition of 2 more equivalents of oxidant, as a test of the deactivation of the catalyst.

At short reaction time, the productivity is directly related to the Ti content. Only the catalyst prepared in ShellSol are less efficient than expected, whereas the catalyst prepared on C₁₈ reversed-phase HPLC silica with the highest amount of Ti (T-C18-1) leads to higher productivity. At longer reaction time (24 h) the productivity is similar in all the catalyst, between 40 and 50 mmol/g, with the same positive exception (T-C18-1) and a very negative exception in the catalyst prepared in ShellSol with the lowest amount of silane (S-L18-1). Productivity at even longer reaction times reaches total values of 55–65 mmol/g (except S-L18-1, which indicates an important degree of deactivation), but now all the catalysts prepared on C₁₈ reversed-phase HPLC silica show improved results (77–80 mmol/g). As the mass of catalyst is fixed in all the experiments, the comparison of TON is more difficult. As expected, the higher Ti content of the catalysts the less TON (Fig. 3), given the lower initial DBT/Ti ratio. However, again the solids prepared in ShellSol show worse performance than the rest of catalysts. More significant is the comparison of the percentage of the maximum possible TON reached with each catalyst. Most of them are able

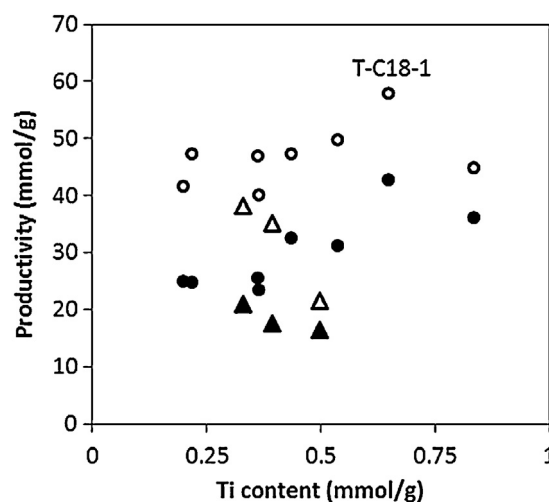


Fig. 2. Productivity (mol of DBT converted per gram of catalyst) vs Ti content of the catalyst: after 3 h (filled symbols) and 24 h (open symbols). Triangles represent catalyst prepared by silanization in ShellSol.

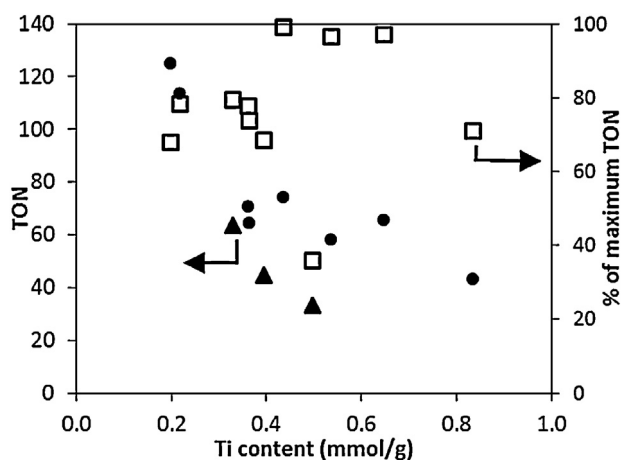


Fig. 3. Relationship between the TON (filled symbols) and the % of the maximum possible TON (open symbols) with the Ti content of the catalysts.

to reach 68–78% of the maximum possible TON, with the same exceptions described above, S-L18-1 that reaches only less than 40% of the maximum, and the three catalysts prepared from C₁₈ reversed-phase HPLC silica, with nearly 100% of the maximum TON,

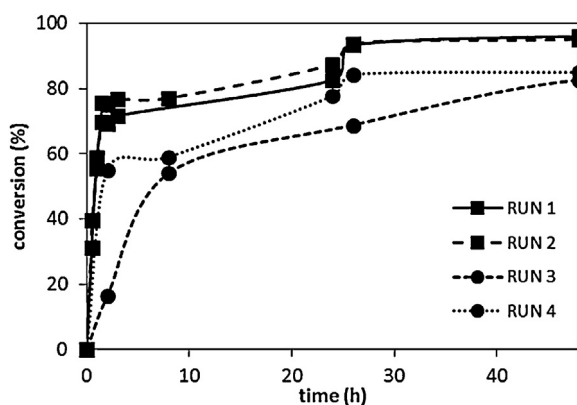


Fig. 4. Reuse of T-C18-1 catalyst in four consecutive runs of DBT oxidation with H_2O_2 .

indicating an optimal use of the oxidant with no deactivation along the time.

The recycling of the two catalysts with the results potentially more interesting was also tested in reactions scaled up 5 times. In the case of T-18H-0.2 the main problem was the loss of around 25% weight of solid in the filtration process, probably due to mechanical attrition of the catalyst. In the case of T-C18-1, the solid is much more resistant and after filtration more than 98% weight was recovered. The results in four consecutive runs are summarized in Fig. 4. In the two first runs conversion with 2 equivalents of H_2O_2 was in both cases around 80% (70–75% conversion in only 2 h), with more than 95% conversion after the addition of 2 more equivalents of oxidant. In the third and fourth runs, those values were slightly lower, around 70% conversion in 24 h and 85% conversion with the additional 2 equivalents of H_2O_2 , demonstrating that productivity can be multiplied by almost 4 in the reuse of the catalyst. When comparing these results with those reported in the literature with Ti catalysts, the oxidant/sulfur ratio is similar (4:1 [42,43]) to, or lower (6:1 [45]) than, other examples, whereas the amount of catalyst is much lower [42] without using an organic co-solvent. Even the conditions described in this work compare well to those used with phosphotungstates, with substrate/catalyst molar ratios from 100 [31] or 120 [33], up to 320 [30], and oxidant/sulfur molar ratios from 2.6 [30] up to values higher than 100 [25,26].

4. Conclusions

Oxidation of dibenzothiophene to the corresponding sulfone in hydrocarbon solution with aqueous hydrogen peroxide can be carried out with titanium heterogeneous catalysts with hydrophobic character. These catalysts are easily prepared from commercial amorphous silica by silanization with long chain silanes (octadecyl or octyl) and then grafting of the titanium sites by reaction with $\text{Ti}(\text{O}^i\text{Pr})_4$. Even they can be prepared from commercially available C_{18} silica. Parameters such as the amount of catalyst and the amount, concentration and addition method of hydrogen peroxide, affect the final result. The productivity per mass of solid or per number of Ti sites can be optimized by tuning the conditions of the catalyst preparation. The possible practical application of the method has been checked by using an industrial grade aromatic hydrocarbon solvent, which has shown to be compatible with both the catalyst preparation and the oxidation reaction. The application of this methodology to the oxidation of real fuel samples is currently under way.

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